



A bipolar electrode cell for aluminium electrorefining

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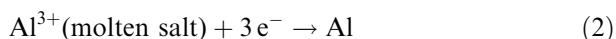
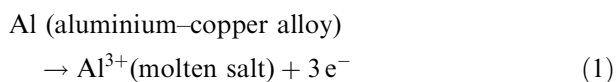
Abstract

Electrorefining of aluminium was carried out at 750 °C using bipolar electrode cells with centre holes 2, 10 or 20 mm in diameter. Through the centre holes liquid electrorefined aluminium rises to the electrolyte surface. The bipolar electrode cell consists of graphite cathodes, Al–Cu–Fe–Mn or Al–Cu–Fe–Zn alloy anodes and a BaCl₂–NaCl–AlF₃–NaF electrolytic melt. The centre hole size of more 20 mm in diameter is required to continuously float up the aluminium electrodeposited onto the electrolyte surface, while the current efficiency of the cell decreases with increase of the centre hole size, from 97% at 2 mm diameter to 92% at 20 mm diameter. Aluminium of 99.97% purity precipitates at the cathode. Iron, manganese and zinc included in the alloy as impurities are hardly deposited and the concentrations of these elements in the deposit are 100, 80 and 170 ppm, respectively. In this process aluminium can be produced with an energy consumption of about 4.9×10^3 kWh (t-Al)⁻¹, which is one-third smaller than that of the Gadeau process.

1. Introduction

Aluminium scrap is usually recycled by remelting with primary aluminium. Although the procedure is not costly, repetition of the remelting process gradually produces lower-grade aluminium alloys. Therefore, it is necessary to develop a new process for aluminium recycling with the aim of reproducing primary aluminium from scrap.

The electrorefining technique has been established by the three-layer process to produce the highest grade (99.999%) aluminium. Electrorefining is described by Equations 1 and 2.



Sullivan and Beauchamp carried out electrorefining of aluminium from scrap aluminium using the three-layer process [1]. Schwarz and Wendt attempted an electrorefining process using a diaphragm to separate pure aluminium from scrap aluminium [2]. Pemsler and Dempsey deposited pure aluminium in a solid state at a relatively low temperature [3]. However, there have been difficulties in current efficiency and energy consumption, when these processes are employed for industrial scale procedures. It is, therefore, necessary

to develop a new process with higher efficiency and lower energy consumption. Previously, we investigated the anodic dissolution of aluminium from aluminium copper alloy into mixed melts of barium chloride (BaCl₂), sodium chloride (NaCl), aluminium fluoride (AlF₃), and sodium fluoride (NaF) to examine the effects of iron, silicon and magnesium included in the scrap as impurities. We further investigated the electrodeposition of aluminium from the melts [4–6]. It was found that iron and silicon did not dissolve into the melt and magnesium dissolved with aluminium; however, the magnesium was hardly deposited cathodically during the electrodeposition of aluminium [6]. In addition we applied a bipolar electrode cell for establishing an efficient system for electrorefining aluminium from aluminium scrap. To float pure liquid aluminium on the melt surface in the bipolar cell we introduced centre holes at the individual bipolar electrodes and the terminal cathode of the bipolar cell.

In this work, we examine the effect of the size of the centre hole of the bipolar electrodes and the terminal cathode on the current efficiency. We determined the minimum centre hole size allowing the liquid aluminium to float up to the melt surface. To survey the effect of the centre hole size on the energy consumption in this bipolar cell, the cell voltage was measured and compared with a value estimated from the cell configuration. Furthermore, to check the effects of the impurities on electrorefining of aluminium, we added iron, manganese

and zinc as impurities into the aluminium copper alloy anode and examined the effects of the impurities on the quality of cathodic electrodeposited aluminium.

2. Experimental details

The cell is depicted schematically in Figure 1. The cell wall was an alumina tube (80 mm inner diameter) inserted into a graphite crucible. The cell itself consisted of a terminal 60 wt % aluminium–copper alloy anode, a terminal graphite cathode, and two bipolar electrodes (77 mm outer diameter, 30 mm thick). It was, therefore, divided into three units. The individual bipolar electrodes and the terminal cathode had a centre hole (2, 10 or 20 mm in diameter), inclined 20°. Two terminal alloy anodes (anode (A) and anode (B)) were employed. Their compositions are listed in Table 1. The anodes were prepared from 99.9% pure aluminium, 99.99% copper, 99.9% iron, manganese and zinc. The upper sides of the bipolar electrodes consisted of the same alloy as the terminal anode and the undersurfaces of graphite. The interelectrode gap was kept at 15 mm by inserting alumina tubes 15 mm in height.

Analytical grade reagents of BaCl_2 , NaCl , AlF_3 and NaF were supplied by Kanto Chemical Company. A 48 mol % BaCl_2 –39% NaCl –5% AlF_3 –8% NaF salt was melted at 750 °C in the crucible containing the terminal anode, and then the bipolar electrodes and the terminal cathode were inserted into the melt. Electrolysis was carried out for 6 h under a constant current at 15 A. Since the bipolar electrode cell had three pairs of anodes and cathodes, the total charge was thus 270 Ah. After electrolysis, the anode alloys on the terminal electrode and the bipolar electrodes were weighed. Further electrodeposited aluminium picked up from the melt surface and in the melt was weighed. The deposit

Table 1. Composition of anode alloys (mass %)

Element	Al	Cu	Fe	Mn	Zn
Anode (A)	61.0	37.3	1.0	0.7	
Anode (B)	60.0	38.0	1.0		1.0

aluminium was dissolved in 6 mol dm^{-3} hydrochloric acid and analysed with ICP emission spectroscopy (Seiko Instruments SPS-3000) to examine the impurity level.

3. Results and discussion

3.1. Purity of electrodeposited aluminium

From analysis of the deposit on the cathode it was found that the purity of the aluminium was higher than 99.97 mass %. The amounts of manganese and iron in the deposit were 0.008 and 0.010 mass %, respectively for the anode alloy (A); zinc and iron accounted for 0.017 and 0.010 mass %, respectively, for the anode alloy (B). In previous work we found that impurities of silicon, iron and magnesium in the anode did not deposit on the cathode. The results demonstrated that the electrorefining from scrap aluminium containing various impurities in this melt recovered pure aluminium.

3.2. Minimum diameter of the centre holes

We examined whether the liquid aluminium deposited could float up to the melt surface through the centre hole. In Table 2 the mass of the aluminium floating up to the melt surface, total mass of the aluminium deposited and decrease in mass of the alloy anode are listed as a function of the centre hole size. The total mass of electrodeposited aluminium is the sum of the aluminium floating up to the melt surface and remaining in the melt between the electrodes. This was almost the same as the decrease of the anode mass. The current efficiency was calculated from the ratio of the total mass to the mass of aluminium equivalent to total electricity. The current efficiency will be discussed in the following Section. For a bipolar cell with a centre hole of 20 mm diameter, the electrodeposited aluminium was able to completely float up to melt surface. For the size of 10 mm, 60% of the electrodeposited aluminium float up but, for the 2 mm hole, no aluminium floated up. It was concluded that a minimum centre-hole diameter of 20 mm is necessary for liquid deposited aluminium to float up to the melt surface.

3.3. Current efficiency

The current efficiency is also shown in Table 2. The mass deposited by a given amount of electricity was calculated with the assumption that all current flows across the bipolar electrode. As seen in Table 2 the

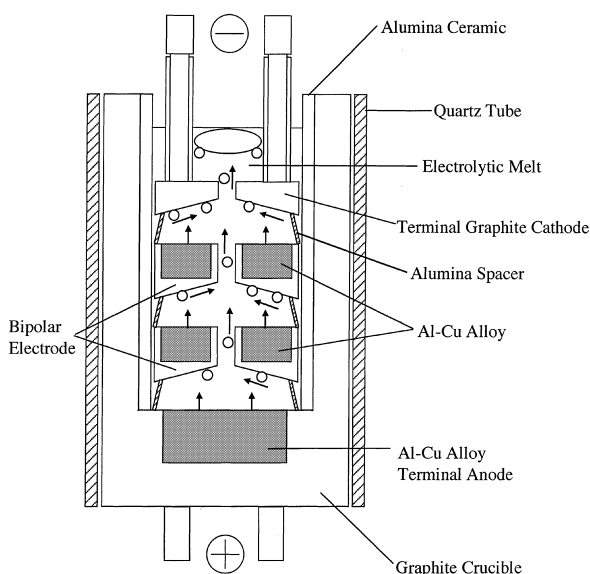


Fig. 1. Schematic illustration of bipolar electrode cell.

Table 2. Mass of aluminium floating up to melt surface, total mass of electrodeposited aluminium and current efficiency with centre hole size in bipolar cell

Centre hole size d/mm	Mass of aluminium floating to melt surface w_f/g	Total mass of electro- deposited aluminium w_d/g	Decrease in mass of the alloy anode w_a/g	Mass of electro- deposited aluminium equivalent to total electricity w_{eq}/g	Current efficiency $\eta/\%$
2	0	88	87	90.0	97
10	51	85	84	89.5	95
20	83	83	83	90.0	92

current efficiency decreases with increase in the centre hole size. Reduction in current efficiency may be explained as due to a bypass currents that directly flow from the terminal anode to the terminal cathode through the centre hole without passing through the bipolar electrodes.

3.4. Cell voltage

The cell voltage was measured and compared with a calculated value. The result is given in Figure 2, where the cell voltage is plotted against current. The cell voltage increases with the increase in centre hole size. This relation between the cell voltage and the centre hole size can be explained by the existence of a bypass current. The cell voltage was calculated from the schematic model described in Figure 3 and the equivalent circuit in Figure 4. By introducing the bypass current the cell voltage can be calculated theoretically and compared with the experimental voltage.

As illustrated in Figure 3 the applied total current (I_T) is divided into a bypass current, I_{by} and a bipolar current, I_{bi} , where the bypass current flows in the melt from the terminal anode to the terminal cathode directly and the bipolar current passes through the bipolar electrodes and the melt. From the equivalent circuit in Figure 4 the relationship among I_T , I_{by} and I_{bi} is described by Equation 3,

$$I_T = I_{bi} + I_{by} \quad (3)$$

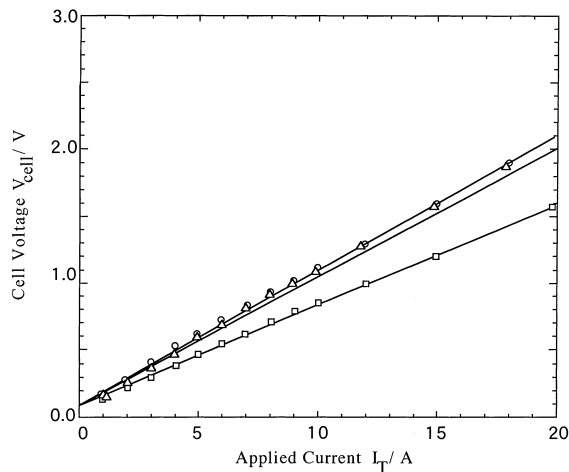


Fig. 2. Current–cell voltage relation for various centre hole size of 2 mm (\square), 10 mm (Δ) and 20 mm (\circ). Calculated relations are solid lines.

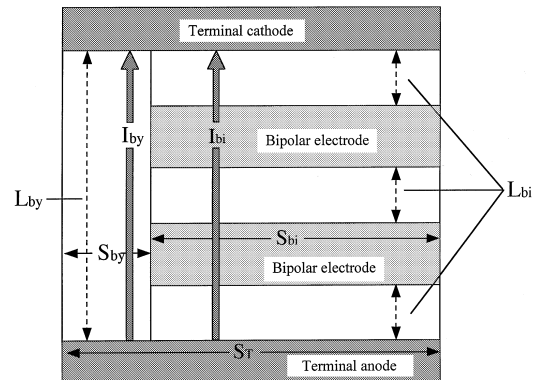


Fig. 3. Calculation model of the bipolar electrode cell. I_{by} : bipolar current flowing through the bipolar electrodes and melts; S_T : cross-sectional area of terminal electrodes; S_{by} : cross-sectional area for I_{by} ; S_{bi} : cross-sectional area for I_{bi} ; L_{by} : distance between the terminal anode and cathode; L_{bi} : distance between the terminal and bipolar electrode and between bipolar electrodes.

The cell voltage during electrolysis consists the thermodynamic potential difference, the activation and concentration overvoltages, and the ohmic potential drop. The activation overvoltage and concentration overvoltage are assumed to be small in this melt as compared with the ohmic potential drop [7, 8]. From the previous study on potential transients using current interruption, it was found that the cell voltage was determined only by the ohmic potential drop in the melt

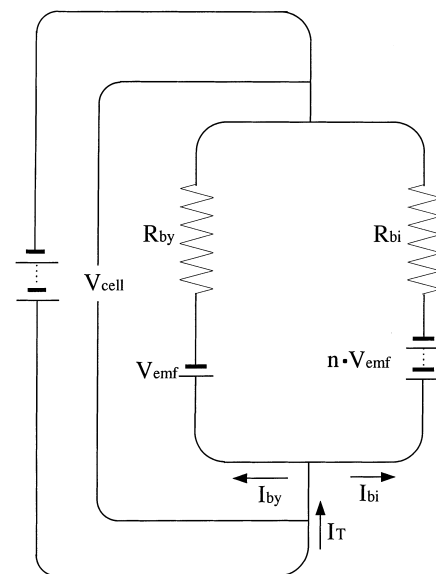


Fig. 4. Equivalent circuit of the bipolar electrode cell.

and the e.m.f. To evaluate the ohmic potential drop, the resistances of the melt R_{by} and R_{bi} in the circuits were calculated as follows:

$$R_{by} = 1/\kappa \times \left(\frac{L_{by}}{S_{by}} \right) \quad (4)$$

$$R_{bi} = 1/\kappa \times n \left(\frac{L_{bi}}{S_{bi}} \right) \quad (5)$$

where κ is the electrical conductivity of the melt, S_{by} is the cross sectional area of the path for bypass current flow, S_{bi} is the area for the bipolar current flow, and n is the number of electrodes. L_{by} and L_{bi} are the distances between the electrodes in the bypass current path and the bipolar current path, respectively. In our previous study, the electrical conductivity, κ of the melt was found to be 2.15 S cm^{-1} [7]. The e.m.f. for a cell consisting of the aluminium–copper alloy and liquid aluminium on the graphite cathode is small and amounts to approximately 0.03 V [4]. Since the bypass current, I_{by} and the bipolar current, I_{bi} are connected in parallel between the terminal electrodes as shown in Figure 3, I_{by} and I_{bi} are described by

$$I_{by} = \frac{V_{cell} - V_{emf}}{R_{by}} \quad (6)$$

$$I_{bi} = \frac{V_{cell} - nV_{emf}}{R_{bi}} \quad (7)$$

From Equations 3, 6 and 7 the cell voltage (V_{cell}) is calculated as a function of the total current, I_T :

$$V_{cell} = \left(\frac{R_{by}R_{bi}}{R_{by} + R_{bi}} \right) I_T + \left(\frac{nR_{by} + R_{bi}}{R_{by} + R_{bi}} \right) V_{emf} \quad (8)$$

The calculated relation between current and cell voltage is shown in Figure 2 by the solid lines. The calculated voltages are in good agreement with the experimental voltage for every centre hole size.

The change in cell voltage with time during electrolysis at 15 A are given in Figure 5(a) and (b) the centre hole sizes of 10 and 20 mm, respectively. The cell voltage initially increases and then decreases and subsequently gradually increases again. The gradual increase in cell voltage may be caused by an increase in interelectrode distance due to the anodic dissolution of the alloy anodes of the bipolar and terminal electrodes. The voltage change in the initial stage may be due to formation of an oxide film due to reaction with impurities such as water or oxygen ions in the melt during the initial stage of electrolysis. The difference in cell voltage between the 10 and 20 mm diameters can be explained from the model in Figure 3 and the equivalent circuit in Figure 4. The change in cell voltage with time can be simulated from the changing interelectrode distance in the following way. From the total electricity, the level of the anode alloy is assumed to drop by

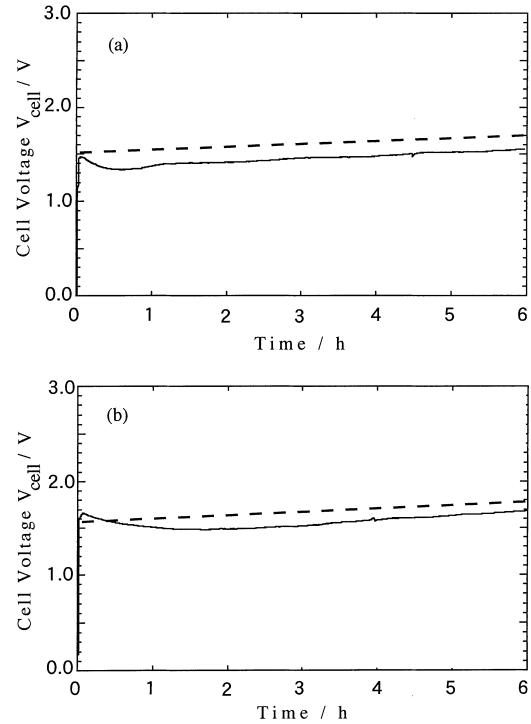


Fig. 5. Comparison between the experimental (—) and calculated (---) cell voltage against time during 15 A electrolysis. Key: (a) centre hole size 10 mm and (b) centre hole size 20 mm.

4.5 mm due to anodic dissolution. The distance between the electrodes therefore changes from the initial value of 15 mm to a final value of 19.5 mm during 6 h of electrolysis. From the changing interelectrode distance and the model in Figure 3, the gradual change in cell voltage was calculated. The calculated results are shown in Figure 5 as dotted lines. The same tendencies are seen between the experimental and calculated cell voltages except for the initial stage of electrolysis. From these results it can be concluded that the cell voltage can be estimated by the e.m.f. of the cell, the electrical conductivity of the melt and the cell configuration.

3.5. Energy consumption

The energy consumption per tonne of aluminium production was also calculated. The result is shown in Table 3 as a function of the size of the centre hole. The energy efficiency was calculated from the average cell voltage and current efficiency during electrolysis at 15 A

Table 3. Cell voltage, current efficiency and energy consumption with centre hole size in bipolar cell during constant current electrolysis at 15 A for 6 h

Centre hole size d/mm	Average cell voltage V_{cell}/V	Current efficiency $\eta/\%$	Energy consumption /kW h (t-Al) ⁻¹
2	1.3	97	4.0×10^3
10	1.4	95	4.4×10^3
20	1.5	92	4.9×10^3

for 6 h. As seen in Table 3, the energy consumption increases with increase in centre hole size. The value of $4.9 \times 10^3 \text{ kWh (t-Al)}^{-1}$ for the 20 mm hole diameter, for example, is one-third smaller than that for the Gadeau process [3].

4. Conclusions

To establish efficient electrorefining of scrap aluminium, bipolar electrode cells were investigated using aluminium alloy anodes and graphite cathodes with centre holes 2, 10 and 20 mm in diameter.

- (i) A centre hole size of over 20 mm diameter is required to continuously float up the aluminium electrodeposited on to the electrolyte surface.
- (ii) When the size of the centre hole increases, however, the current efficiency of the bipolar cell decreases.
- (iii) Cell voltages calculated from the e.m.f. and the conductivity of the melt agree closely with experimental values.
- (iv) In this process 99.97% pure aluminium deposits on the cathode, but iron, manganese and zinc included in the anode alloys hardly deposit on the cathode.

- (v) Pure aluminium can be reproduced from aluminium scrap with an energy consumption of about $4.9 \times 10^3 \text{ kWh (t-Al)}^{-1}$ using the present bipolar cell system.

References

1. T.A. Sullivan and R.L. De Beauchamp, 'Recovery of Aluminium Base and Precious Metal from Electronic Scrap', Bureaux des Mines, RI-7617, BP-2090 (1971).
2. V. Schwarz and H. Wendt, *J. Appl. Electrochem.* **25** (1995) 34.
3. J.P. Pemsler and M. Dempsey, 'Electrorefining of Aluminium', Gouv. Rep. Announe, NSF/CPE-81012, B.P.81-243693 (1981).
4. M. Ueda, S. Konda, T. Sasaki and T. Ishikawa, in R.T. Carlin, S. Deki, M. Matsunaga, D.S. Newman, J.R. Selman and G.R. Stafford (Eds), Tenth International Symposium on 'Molten Salt', 1996, The Electrochemical Society Proceedings Series, Pennington, NJ (1996), p. 229.
5. M. Ueda, S. Konda, T. Sasaki and T. Ishikawa, in H. Wendt (Ed), 'Molten Salt Chemistry and Technology 5' (Trans Tech Publications, Switzerland, 1998), p. 303.
6. M. Ueda, S. Konda, T. Sasaki and T. Ishikawa, *Denki Kagaku* **66** (1998) 164.
7. M. Ueda, S. Konda, T. Sasaki and T. Ishikawa, *Denki Kagaku* **64** (1996) 978.
8. S. Konda, T. Sasaki and T. Ishikawa, *Denki Kagaku* **64** (1996) 1090.